THE SPECTROPHOTOMETRIC DETERMINATION OF ELEMENTS WITH CHROMAZUROL S IN THE PRESENCE OF CETYLTRIMETHYLAMMONIUM BROMIDE AND TRITON X-100.

II. MULTICOMPONENT SPECTROPHOTOMETRIC DETERMINATION OF THE SUM OF THE RARE EARTH ELEMENTS, Al, Fe AND Th USING MULTIVARIATE CALIBRATION WITH PLS DATA EVALUATION

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A procedure was developed for the simultaneous spectrophotometric determination of the sum of the rare earth elements, Al, Fe and Th using chromazurol S in the presence of cetyltrimethylammonium bromide and Triton X-100 for optimized conditions at pH 5.5 and 10.2. Multivariate calibration and the PLS procedure were employed to evaluate data for a variable number of calibration solutions and wavelengths. A new procedure was described for combination of the data of independently measured systems at both pH values. The errors in the determination of the concentration values for Al, Fe, Th and the sum of the rare earth elements in model solutions and in the concentrates of the rare earth elements were not greater than 10 rel.%.

It was found that the multicomponent determination of the metal ions can be readily carried out by spectrophotometric multicomponent analysis of a mixture of these ions in the form of their chelates with sensitive organic reagents using the efficient multivariate calibration and Partial Least Squares (PLS) methods for data evaluation, even for components with very similar spectral characteristics in the visible region[1 – 3]. It was found that errors in the prediction of the results (values of the concentrations of the individual components in unknown solutions) are greatly dependent on the shape of the statistic plan of the calibration set used, the number of calibration solutions and the selected weighed set of wavelengths[2].

In this work, a procedure is recommended for the simultaneous determination of the rare earth elements (REE), Al, Fe and Th using chromazurol S (CAS) in the presence of cetyltrimethylammonium bromide (CTMA) and Triton X-100 under defined conditions in the acidic and alkaline regions. The smallest errors were achieved in the determination of the concentrations of the individual metal ions for the set of spectrophotometric data obtained by the combination of two completely independent measured systems at pH 5.5 and 10.2. Such a procedure has not yet been described in the literature in connection with the application of PLS and permits the determination of Al, Fe and Th impurities in concentrates of the rare earth elements. In order to obtain reliable results, it is necessary to have not only detailed knowledge of the conditions for the interaction of the individual cations with the reagent in the presence of the tenside, but also to determine compromise optimal conditions for multicomponent analysis of cation mixtures.

This work is a continuation of an earlier work[4], describing a detailed study of the interactions of the ions of the lanthanoids, La and Y with CAS in the presence of CTMA and Triton X-100.

The reactions of CAS in the presence of various cationic tensides with REE cations, Al^{3+}, Fe^{3+} and Th^{4+} have already been discussed in a number of works: REE (refs[5 - 13]), Al^{3+} (refs[14 - 29]), Fe^{3+} (refs[30 - 32]) and Th^{4+} (refs[33 - 35]). However, the authors of these works proposed various reaction mechanisms and the optimal conditions for the determination of the individual elements were often very different. Thus, we once again found optimal conditions for the reactions of Al^{3+}, Fe^{3+} and Th^{4+} with CAS in the presence of tensides, and the conditions found in the previous Part I (ref.[4]) were used to determine the REE.

As the complexes of the test metal cations with CAS in the presence of tensides have similar optical characteristics[4 - 35], their simultaneous determination is practically possible only using effective methods of multivariate calibration. The PLS method has been found very useful for this purpose[36], as it eliminates some of the limitations of other methods that are frequently used in practice, such as Multiple Linear Regression (MLR) and Principal Component Regression (PCR), especially in the presence of interactions between the test components or for considerable overlap of the absorbance bands of their complexes or for deviations from the Bouguer–Lambert–Beer law. Calculations by the PLS method, similar to the other methods of multivariate calibration, are carried out in two basic steps. In the first step (calibration) a search is made for a relationship between the data (absorbance) matrix with elements A_{np} (n is the number of calibration mixtures (solutions) and p is the number of wavelengths) and the concentration matrix with elements C_{nm} (m is the number of components determined). In the second step (prediction) the values of the concentrations of the individual components are determined in the sample. These concentrations are calculated from the measured sample absorbance values using the relationship found in the calibration phase. The algorithm and mathematical basis of the PLS method are described in detail in refs[36 - 40].

EXPERIMENTAL

Chemicals

The stock solution of Th^{4+} with a concentration of 0.15 mol l^{-1} in 0.1 M HNO_3 was prepared from the substance supplied by the Schuchardt Co., Germany.

The stock solutions of the metal ions of the rare earth elements with concentrations of 0.05 mol l^{-1} in 0.1 M HNO_3 were prepared by dissolving a defined weight of the nitrates (La, Nd) or oxide (Sc) from the Soyuzkhimexport Co. C.I.S., or by diluting a standard Ce^{3+} solution with a concentration of 0.5 mol l^{-1} from the Loba Chemie Co., Austria.

These solutions were standardized by titration with EDTA over xylenol orange at pH 5.0 – 5.5 (urotropine buffer).

The stock solutions of Al^{3+} with a concentration of 0.15 mol l^{-1} in 1 M HCl and Fe^{3+} with a concentration of 0.2 mol l^{-1} in 0.4 M HCl were prepared by dissolving the appropriate p.a. purity metal obtained from the Panenské Břežany Co., The Czech Republic (Al) and the CIBA Co., Switzerland (Fe) in concentrated HCl, filtering and diluting with water. These two solutions were standardized by back titration of EDTA with a $Pb(NO_3)_2$ solution over xylenol orange at pH 5.0 – 5.5 (urotropine buffer).

The diluted stock solutions of the individual metals with a concentration of 250 μmol l^{-1} in 0.1 M HNO_3 were determined by diluting the above concentrated stock solutions and were used to prepare the working solutions within three weeks.

Pyridine buffer with a concentration of 1 mol l^{-1} and the required pH value was prepared from the redistilled substance with p.a. purity from the Hajduki Co., Poland.

The other chemicals and instruments employed are described in the previous Part I (ref.[4]).

Preparation of Working Solutions

The individual working solutions were pipetted in the order: an acidic solution of the test metal ion or a mixture of test ions, a solution of the interfering substance or inert salt, an HNO_3 solution to adjust the ionic strength, the tenside solution and the reagent solution. For measurements at pH 5.5, 0.1 mol l^{-1} pyridine buffer was added, while 5 mol l^{-1} NH_3 (ammonia buffer) was added for measurements at pH 10.2. The pH was precisely adjusted by small additions of variously concentrated NH_3 solutions so that the volume change was not greater than 1%.

Evaluation of Data

The calibration dependences were drawn up by regression analysis using the STAT90 program[41].

Multicomponent analysis was carried out using the PLS-G program[38,42]. The number of significant main components in the PLS algorithm was determined by cross-validation[43]. Various calibration sets were selected on the basis of the literature data[44].

The basic criterium for correctness of the results obtained by calculation using the PLS program is agreement of the actual (given) concentrations of the individual components with the calculated (predicted) values. This can be expressed by the component relative prediction error (CRPE) and the average relative prediction error for all the components and test solutions (MRPE – Multicomponent Relative Prediction Error):

$$\mathrm{CRPE}_j = \sqrt{\sum_{i=1}^{T} (c_{ij} - \hat{c}_{ij})^2 \Big/ \sum_{i=1}^{T} c_{ij}^2} \;.\; 100 \qquad [\%] \qquad (1)$$

$$\mathrm{MRPE} = \Big[\sum_{i=1}^{T} \sqrt{\sum_{j=1}^{M} (c_{ij} - \hat{c}_{ij})^2 \Big/ \sum_{j=1}^{M} c_{ij}^2} \;\Big] \;.\; T^{-1} \;.\; 100 \qquad [\%], \qquad (2)$$

where T is the number of test solutions (samples), M is the number of components, c_{ij} and $\hat{c}_{ij}$ are the given and calculated concentration values for the individual components.

The calculation was carried out on the IBM PC/AT compatible computer.

RESULTS AND DISCUSSION

Interaction of the Al^{3+}, Fe^{3+} and Th^{4+} Ions with CAS in the Presence of CTMA

The information given for optimal conditions for the individual Al–CAS–CTMA, Fe–CAS–CTMA and Th–CAS–CTMA systems given in the literature was verified (c_L = 20 – 50 μmol l^{-1}, pH 4 – 7); however, for the multicomponent analysis, new (compromise) conditions has to be found that would be optimal for simultaneous determination of all three ions. First the absorption spectra were measured for the individual ternary systems for $c_{Al} = c_{Fe} = c_{Th}$ = 5 μmol l^{-1}, c_L = 30 μmol l^{-1}, c_{CTMA} = 120 and 1 200 μmol l^{-1}, and 0.1 mol l^{-1} pyridine buffer in the pH range 4.77 – 6.22 and wavelength region 350 – 750 nm. Then the absorbances of the individual ternary complexes and of the blank were measured at wavelengths of 600 – 650 nm for the above metal concentrations, c_L = 20 mmol l^{-1}, pH 4.77, 5.02, 5.27, 5.66, 5.95, 6.22 and c_{CTMA} = 80, 120, 200, 400, 800, and 1 200 μmol l^{-1}. The absorbance differences were calculated from the values obtained, measured 15 min after addition of the buffer and optimal conditions were found for the determination of the individual metals in the separate systems.

The choice of a suitable buffer was studied in the Th–CAS–CTMA system for concentrations of c_{Th} = 5 μmol l^{-1}, c_L = 20 μmol l^{-1}, c_{CTMA} = 800 μmol l^{-1}, pH = 5.0, and 610 nm. Acetate and succinic buffers interfere at concentrations of 20 mmol l^{-1}. Urotropine and pyridine buffers do not interfere even at a concentration of 0.2 mol l^{-1}. Subsequent work was carried out using the pyridine buffer as the urotropine buffer was not sufficiently stable (changes in the adjusted pH values of the stock solutions were observed 2 days after preparation).

The Al–CAS–CTMA System

The absorption spectra for lower and higher CTMA concentrations are depicted by curves *1* in Figs 1*a* and 1*b*.

The determined optimal conditions for the determination of Al are as follows: c_L = 20 μmol l^{-1}, c_{CTMA} = 300 – 800 μmol l^{-1}, pH = 5.4 – 5.8 (0.1 mol l^{-1} pyridine buffer). Maximum absorbance is achieved for 620 – 630 nm, 15 min after addition of the buffer and is constant for at least 30 min. At higher CTMA concentrations, the absorbance values for pH > 6 and pH < 5 decrease rapidly.

The parameters of the calibration dependences calculated for Al concentrations in the range c_{Al} = 0 – 8 μmol l^{-1}, are given in Table I. The calibration curve is linear in the Al concentration range c_{Al} < 6 μmol l^{-1}.

The Fe–CAS–CTMA System

In the Fe–CAS–CTMA system, the λ_{max} value shifts with increasing pH and CTMA concentration from 625 to 655 nm. The absorption spectra in the ternary system at lower and higher CTMA concentrations are depicted by curves *2* in Fig. 1.

The optimal conditions for the formation of the ternary associates with Fe are as follows: c_L = 20 μmol l^{-1}, c_{CTMA} = 400 – 1 200 μmol l^{-1}, pH 5.3 – 5.7 (0.1 mol l^{-1} pyridine buffer), λ_{max} = 645 – 655 nm, the absorbance becomes constant 15 min after addition of the buffer and remains constant for at least 30 min.

The parameters of the calibration dependence calculated for the concentration range c_{Fe} = 0 – 8 μmol l^{-1} are given in Table I. The calibration curve is linear in the concentration range c_{Fe} < 6 μmol l^{-1}.

The Th–CAS–CTMA System

In the Th–CAS–CTMA system, the λ_{max} value shifts from 605 to 615 nm with increasing pH and c_{CTMA}; however, at pH > 6 the ion associate rapidly decomposes with increasing CTMA concentration. The absorption spectra for lower and higher CTMA concentrations are depicted in Fig. 1, curves *3*. The optimal conditions for the formation of the ternary associates with Th are as follows: c_L = 20 μmol l^{-1}, c_{CTMA} = 120 – 400 μmol l^{-1}, pH 5.3 – 5.8 (0.1 mol l^{-1} pyridine buffer), λ_{max} = 605 – 615 nm. The absorbance becomes constant 10 min after addition of the buffer and remains constant for at least 15 min.

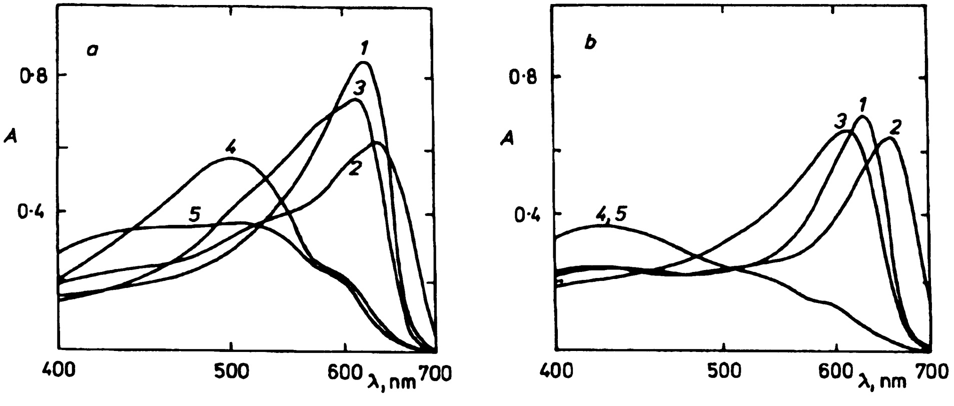

FIG. 1

The absorption spectra of Al^{3+}, Ce^{3+}, Fe^{3+}, and Th^{4+} with CAS (30 μmol l^{-1}) in the presence of CTMA. pH 5.5 (0.1 mol l^{-1} pyridine buffer). c_{CTMA} = 120 μmol l^{-1} (*a*), 1.2 mmol l^{-1} (*b*); c_M (μmol l^{-1}): *1* Al^{3+}, 4.99; *2* Fe^{3+}, 4.99; *3* Th^{4+}, 5.00; *4* Ce^{3+}, 5.17; *5* blank

The parameters of the calibration dependence calculated for the concentration range c_{Th} = 0 – 8 μmol l^{-1} are given in Table I. The calibration curve is linear in the concentration range $c_{Th} < 6$ μmol l^{-1}.

On the basis of these results, conditions can be found in the pH range 4.7 – 6.0 and at c_{CTMA} = 120 – 1 200 μmol l^{-1} to permit the determination of all three elements even in the presence of an excess of the rare earth element ions (see below).

Determination of Al in the Presence of Ce

At a ratio of $c_{CTMA}/c_L \approx 3$, the presence of Ce^{3+} at pH 5 – 6 produces a similar change in the spectrum of the reagent as a decrease in the pH, i.e. preference for the H_2L^{2-} form of the reagent with λ_{max} = 520 nm. However, at pH 5.5 the strongly absorbing ternary associate Ce–CAS–CTMA with λ_{max} = 625 nm or 650 nm is not yet formed, see curves *4* and *5* in Fig. 1*a*.

At higher CTMA concentrations, c_{CTMA} = 1.2 mmol l^{-1}, there is no change in the spectrum of the reagent (curves *4* and *5* in Fig. 1*b* coalesce). These facts can be utilized in the determination of Al^{3+} in the presence of excess Ce or some other lanthanide under optimal conditions c_L = 20 μmol l^{-1} , c_{CTMA} = 400 μmol l^{-1}, pH 5.4 (0.1 mol l^{-1} pyridine buffer).

The parameters of the calibration dependence calculated for the Al concentration range c_{Al} = 0 – 8 μmol l^{-1} in the presence of excess Ce^{3+}, c_{Ce} = 0.5 mmol l^{-1} are given in Table I. The calibration curve is linear in the concentration range $c_{Al} < 5.7$ μmol l^{-1}.

TABLE I

Parameters of the calibration dependences of the Al, Fe and Th ions in the metal–CAS–CTMA system

Parameter	Al		Fe	Th
c_L, μmol l^{-1}	20		20	20
c_{CTMA}, μmol l^{-1}	400		800	120
pH	5.4		5.6	5.7
λ, nm	620		650	610
$\varepsilon \pm s$, l mol^{-1} cm^{-1}	127 700 ± 400	127 500 ± 360[a]	117 100 ± 330	124 000 ± 600
$q \pm s_q$[b]	0.057 ± 0.005	0.076 ± 0.005[a]	0.010 ± 0.003	0.067 ± 0.005
$A_{blank} \pm s_{blank}$[c]	0.049 ± 0.001	0.071 ± 0.001[a]	0.014 ± 0.002	0.063 ± 0.002
c_{lim}, μg ml^{-1}[d]	–	0.005[a]	–	–

[a] The Al–CAS–CTMA system in the presence of excess Ce^{3+} with a concentration of c_{Ce} = 0.5 mmol l^{-1}; [b] intercept on the absorbance axis; [c] number of points on the calibration dependence, number of blank values (n = 10); [d] detection limit[45]: $c_{lim} = 10 \cdot s_{blank} \cdot 1\,000 \cdot M_r/\varepsilon$.

On the basis of the above-determined conditions, Al can be determined in the presence of Ce^{3+} (or some other lanthanide) at a ratio of mass concentrations of ρ_{Ce}/ρ_{Al} < 1 300.

Analogous conclusions are valid for Fe and Th; however, the optimal values for the determination of Fe^{3+} are c_{CTMA} = 800 μmol l^{-1}, pH 5.6 (0.1 mol l^{-1} pyridine buffer) and for the determination of Th^{4+} c_{CTMA} = 120 μmol l^{-1} , pH = 5.7 (0.1 mol l^{-1} pyridine buffer).

Multicomponent Analysis

Calibration and Testing Sets

Measurements in the individual systems at pH 5.5 and 10.2 were carried out and evaluated for 3 independent calibration sets. Combination of the data for these systems (pH 5.5 + pH 10.2) yielded further two calibration sets, which were also evaluated.

A) *The complete factor plan 3^3* (27 solutions) for the 3 test components was selected so that combination of the set for Al, Fe and Th at pH 5.5 and the set for Fe, Th and REE at pH = 10.2 could yield the partial factor plan 3^{4-1} for 27 solutions for simultaneous determination of all 4 components.

B) *The complete factor plan with a central point $2^3 + 1$* (9 solutions) for 3 test components as in the previous case was selected so that the combination of the two calibration sets could yield a partial factor plan with a central point $2^{4-1} + 1$ for 9 solutions for simultaneous determination of 4 components.

C) *The Box-Behnken plan (BBP)*, 12 solutions for 3 test components.

Table II gives selected calibration sets and the testing set (symbols 1, 0, −1, 0.5 and −0.5 represent coded concentration levels). The actual concentration levels of the individual components are given in Table III. The upper concentration values of the individual components in the calibration solutions were selected so that the corresponding absorbances attained a value of 0.5 – 0.6 for one component (the absorbance then had a value of ≈ 1.7 for a calibration solution with the upper concentration levels of all three components). The low concentration levels of the components were set so that the absorbance value for a single component corresponded to approximately 3 – 4 times the absorbance value for the reagent–tenside binary system.

Selection of Wavelengths

The wavelengths at which the measurement was carried out were selected on the basis of Figs 1*b* and 2 to include at least those wavelengths at which maximum absorbance is achieved for the complexes of the individual components. At points where there is considerable spectral overlap, the wavelengths were selected close together, while the intervals between the individual wavelengths were larger at the edges of the spectral bands. The absorbance of each calibration solution was measured for 18 wavelengths for each of the separate systems, i.e. for pH 5.5 and pH 10.2. The combined system pH 5.5 + 10.2 then contained the absorbance of each system at 36 wavelengths. Then the number of wavelengths was reduced in an attempt to limit as far as possible the number of measurements while retaining sufficient correctness of the results. Table IV gives a survey of the wavelengths and their concrete values.

TABLE II
Calibration sets 3^3, 3^{4-1} (*a*) and $2^3 + 1$, $2^{4-1} + 1$ (*b*), BBP (*c*) and the testing set (*d*)

Solution	Al	Fe	Th	REE	Solution	Al	Fe	Th	REE
		(*a*)					(*b*)		
1	1	1	1	1	1	1	1	1	1
2	0	1	1	0	2	-1	1	1	-1
3	-1	1	1	-1	3	1	-1	1	-1
4	1	0	1	-1	4	-1	-1	1	1
5	0	0	1	0	5	1	1	-1	-1
6	-1	0	1	1	6	-1	1	-1	1
7	1	-1	1	-1	7	1	-1	-1	1
8	0	-1	1	0	8	-1	-1	-1	-1
9	-1	-1	1	1	9	0	0	0	0
10	1	1	0	1			(*c*)		
11	0	1	0	0	1	0	1	1	0
12	-1	1	0	-1	2	1	0	1	1
13	1	0	0	-1	3	-1	0	1	-1
14	0	0	0	0	4	0	-1	1	0
15	-1	0	0	1	5	1	1	0	1
16	1	-1	0	1	6	-1	1	0	-1
17	0	-1	0	0	7	1	-1	0	1
18	-1	-1	0	-1	8	-1	-1	0	-1
19	1	1	-1	-1	9	0	1	-1	0
20	0	1	-1	0	10	1	0	-1	1
21	-1	1	-1	1	11	-1	0	-1	-1
22	1	0	-1	-1	12	0	-1	-1	0
23	0	0	-1	0			(*d*)		
24	-1	0	-1	1	1	0.5	-0.5	-0.5	0.5
25	1	-1	-1	1	2	-0.5	0.5	0.5	-0.5
26	0	-1	-1	0	3	-0.5	-0.5	0.5	-0.5
27	-1	-1	-1	-1	4	0.5	0.5	-0.5	0.5

Two basic series of measurements were carried out:

1. *Model sample.* The REE ions consist of a mixture of Ce^{3+} (45 mole %), La^{3+} (33 mole %) and Nd^{3+} (22 mole %), which roughly corresponds to the ratio of the main REE in hydroxide concentrates.

2. *Practical samples.* A dilute solution of the reference hydroxide concentrate 086/85 solution[4].

Al^{3+}, Fe^{3+} and Th^{4+} were added to both series from the standard solutions.

TABLE III
Concentrations of ions in model sample and in sample of hydroxide concentrates of rare earth elements I and II

Symbol	c, μmol l^{-1}					
	Al	Fe	Th	REE[a]		
				model sample	sample I	sample II
-1	0.442	0.443	0.447	0.665	0.653	910.0
0	1.325	1.330	1.340	1.990	1.958	910.0
1	3.974	3.990	4.020	5.987	5.874	910.0
-0.5	0.768	0.771	0.777	1.158	1.136	910.0
0.5	2.296	2.305	2.322	3.459	3.394	910.0

[a] Concentrate[4] was diluted to that the concentration of the sum of the REE corresponded to the concentration order of the other test elements (sample I) or was about 1 000 times higher (sample II).

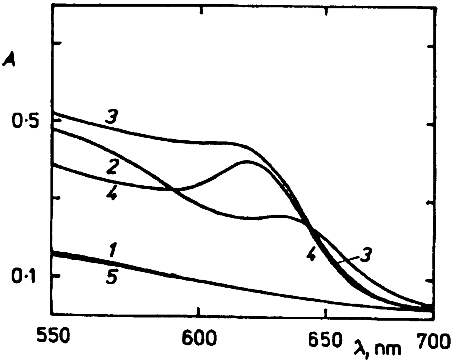

FIG. 2
The absorption spectra of Al^{3+}, Ce^{3+}, Fe^{3+}, and Th^{4+} with CAS (143 μmol l^{-1}) in the presence of CTMA (312 μmol l^{-1}) and Triton X-100 (0.016 wt.%). pH 10.2 (ammonia buffer). c_M (μmol l^{-1}): *1* Al^{3+}, 4.99; *2* Fe^{3+}, 4.99; *3* Th^{4+}, 5.00; *4* Ce^{3+}, 5.17; *5* blank

Simultaneous Determination of Al, Fe and Th at pH 5.5 (in the Presence of the Rare Earth Elements)

The following compromise conditions are suitable for the simultaneous determination of Al^{3+}, Fe^{3+} and Th^{4+} in a total maximal concentration of $c_{\mathrm{M}} = 12\ \mu\mathrm{mol\ l^{-1}}$: $c_{\mathrm{L}} = 30\ \mu\mathrm{mol\ l^{-1}}$, $c_{\mathrm{CTMA}} = 1\,200\ \mu\mathrm{mol\ l^{-1}}$, pH 5.5 (0.1 mol $\mathrm{l^{-1}}$ pyridine buffer).

At this tenside concentration and pH value, the various maximum positions for the individual ternary complexes are as follows: Th^{4+} 606 nm, Al^{3+} 625 nm, and Fe^{3+} 653 nm; these positions were utilized for the multicomponent determination of these elements. An increased reagent concentration for the multicomponent determination compared to the above optimal conditions for the individual cations is necessary for the quantitative formation of all the ternary complexes in the mixture, but leads to increased curvature of the calibration dependence at low metal ion concentrations. Because of the higher reagent concentration, the optimal tenside concentration is also higher. The absorbance was measured against water 15 min after addition of the pyridine buffer. Under these conditions, the REE ions did not affect the results (see Fig. 1*b*).

TABLE IV

Survey of the numbers of wavelengths and their values for the evaluated data sets

System, pH	No. of λ	λ, nm
5.5	18	540, 550, 560, 570, 580, 600, 610, 620, 630, 640, 650, 660, 665, 670, 675, 680, 685, 690
5.5	9	550, 570, 600, 620, 640, 660, 670, 680, 690
10.2	18	570, 580, 590, 595, 600, 605, 610, 615, 620, 625, 630, 635, 640, 645, 650, 655, 660, 665
10.2	9	580, 595, 605, 615, 625, 635, 645, 655, 665
5.5	36	540, 550, 560, 570, 580, 600, 610, 620, 630, 640, 650, 660, 665, 670, 675, 680, 685, 690
10.2		570, 580, 590, 595, 600, 605, 610, 615, 620, 625, 630, 635, 640, 645, 650, 655, 660, 665
5.5	18	550, 570, 600, 620, 640, 660, 670, 680, 690,
10.2		580, 595, 605, 615, 625, 635, 645, 655, 665
5.5	10	550, 600, 640, 670, 690,
10.2		580, 605, 625, 645, 665

The results of the calculations for various calibration sets and sets of wavelengths for the model sample and practical samples of hydroxide concentrates of rare earth elements are given in Tables V and VI.

Simultaneous Determination of Fe, Th and REE at pH 10.2 (in the Presence of Al)

The simultaneous determination of Fe, Th and the sum of REE with a total maximum concentration of $c_M = 14$ μmol l^{-1} was carried out using a mixture of tensides $c_{CTMA} = 312$ μmol l^{-1} and $w_{Triton} = 0.016$ wt.%, $c_L = 143$ μmol l^{-1} and pH 10.2 (ammonia buffer). These conditions are optimum for the formation of the ternary complexes of the rare earth elements and were taken from Part I (ref.[4]). Under these conditions, the ternary complexes of Al^{3+}, Fe^{3+} and Th^{4+} are also formed (see Fig. 2). However, the ternary associate of Al^{3+} is rapidly hydrolyzed and, for $c_{Al} < 10$ μmol l^{-1}, the spectrum consists practically only of the absorption of the reagent 3 min after adjusting the pH value, i.e. Al^{3+} has no effect. The associates of Fe^{3+} and Th^{4+} with $\lambda_{max} = 615$ nm or 634 nm, respectively, are stable in time, but their absorbance decreases with increasing pH value (pH > 10.3). The Ce^{3+} associate, $\lambda_{max} = 624$ nm, exhibits a decrease in absorbance of only −0.17% per min, so that the measurement was carried out 5 min after adjusting the pH, against water as a blank. Every attempt to change the above optimal conditions leads to increased instability of the system.

The results of the calculations for various calibration sets and sets of wavelengths for model samples and practical samples of hydroxide concentrates of the rare earth elements are given in Tables V and VI.

TABLE V
CRPE and MRPE values in dependence on the number of calibration solutions for 18 or 36 (combined system) wavelengths
Model sample

No. of solutions	pH 5.5				pH 10.2				pH 5.5 + pH 10.2				
	CRPE, %			MRPE %	CRPE, %			MRPE %	CRPE, %				MRPE %
	Al	Fe	Th		Fe	Th	REE		Al	Fe	Th	REE	
27	7.8	3.6	5.6	5.4	5.4	6.5	3.4	4.6	7.5	3.4	5.2	4.3	5.2
9	9.0	7.7	6.6	7.1	9.8	9.0	5.2	7.7	8.7	6.9	8.1	5.5	7.4
12	9.9	7.8	8.9	8.3	8.0	10.6	6.2	7.8	–	–	–	–	–

TABLE VI
CRPE and MRPE in dependence on the number of wavelengths
(*a*) *Model sample* (27 calibration solutions)

No. of λ	pH 5.5				pH 10.2				pH 5.5 + pH 10.2				
	CRPE, %			MRPE %	CRPE, %			MRPE %	CRPE, %				MRPE %
	Al	Fe	Th		Fe	Th	REE		Al	Fe	Th	REE	
36	–	–	–	–	–	–	–	–	7.5	3.4	5.2	4.3	5.2
18	7.8	3.6	5.6	5.4	5.4	6.5	3.4	4.6	6.3	8.4	8.1	7.2	7.2
10	–	–	–	–	–	–	–	–	8.1	5.6	5.0	4.7	6.5
9	9.2	5.7	7.2	7.1	6.9	7.9	5.6	6.5	–	–	–	–	–

(*b*) *Model sample* (9 calibration solutions)

No. of λ	pH 5.5				pH 10.2				pH 5.5 + pH 10.2				
	CRPE, %			MRPE %	CRPE, %			MRPE %	CRPE, %				MRPE %
	Al	Fe	Th		Fe	Th	REE		Al	Fe	Th	REE	
36	–	–	–	–	–	–	–	–	8.7	6.9	8.1	5.5	7.4
18	9.0	7.7	6.6	7.1	9.8	9.0	5.2	7.7	9.2	7.9	8.9	6.0	8.1
10	–	–	–	–	–	–	–	–	9.6	8.7	9.2	6.9	8.7
9	9.8	8.5	8.6	8.6	10.5	9.9	7.0	8.9	–	–	–	–	–

(*c*) *Practical sample REE I* (27 calibration solutions)

No. of λ	pH 5.5				pH 10.2				pH 5.5 + pH 10.2				
	CRPE, %			MRPE %	CRPE, %			MRPE %	CRPE, %				MRPE %
	Al	Fe	Th		Fe	Th	REE		Al	Fe	Th	REE	
36	–	–	–	–	–	–	–	–	8.2	6.6	4.8	5.4	6.8
18	6.5	4.7	6.5	5.6	6.9	6.9	5.1	6.1	7.3	5.6	8.4	6.2	7.3
10	–	–	–	–	–	–	–	–	8.9	6.6	7.2	5.7	7.2
9	8.9	5.2	7.9	7.4	8.9	8.1	6.5	7.9	–	–	–	–	–

Table VI
(*Continued*)
(*d*) *Practical sample REE I* (9 calibration solutions)

No. of λ	pH 5.5				pH 10.2				pH 5.5 + pH 10.2				
	CRPE, %			MRPE %	CRPE, %			MRPE %	CRPE, %				MRPE %
	Al	Fe	Th		Fe	Th	REE		Al	Fe	Th	REE	
36	–	–	–	–	–	–	–	–	7.7	6.7	7.0	9.2	7.5
18	8.5	9.5	8.7	8.9	9.7	9.2	6.2	7.7	6.7	7.5	7.0	7.2	6.7
10	–	–	–	–	–	–	–	–	8.5	8.7	8.0	10.5	8.7
9	8.7	9.9	6.2	9.0	6.8	8.5	6.2	7.2	–	–	–	–	–

(*e*) *Practical sample REE II* (9 calibration solutions)

No. of λ	pH 5.5			
	CRPE, %			MRPE, %
	Al	Fe	Th	
18	9.2	6.2	8.6	7.8
9	7.5	6.5	7.5	7.2

Multicomponent Determination of Al, Fe, Th and the REE for Combined Data for the Systems at pH 5.5 and 10.2

At pH 5.5 and under the above conditions, Al^{3+}, Fe^{3+} and Th^{4+} can be determined, while only Fe^{3+}, Th^{4+} and the sum of the REE can be determined at pH 10.2. Simultaneous evaluation of information on both systems (combination of the data measured at both pH values) permits determination of unknown concentrations of all these four components, Al, Fe, Th and the sum of the REE, without solving the two three-component systems separately.

The results of the calculations for various calibration sets and sets of wavelengths for model sample and practical samples of hydroxide concentrates of the rare earth elements are given in Tables V and VI.

Analysis of the Model Sample

A model series was employed to test the possibility of simultaneous determination of the REE, Al, Fe and Th. The advantages and disadvantages of the individual selected calibration sets, the relative errors in the prediction of the concentrations of the individual components, the possibility of combining the data measured separately at various pH values into a single data set and the possibility of reducing the number of wavelengths in the individual systems and in the combined system were evaluated.

The Suitability of Selection of Calibration Sets

The best results, i.e. the lowest values of the CRPE and MRPE, at both the pH values, were achieved for a calibration set of 27 solutions. It would seem advantageous to decrease the number of calibration solutions to 9, as the MRPE value is increased only by 1.7 rel.% (pH 5.5), 3.1 rel.% (pH 10.2) or 2.2 rel.% (combined system). The use of the Box–Behnken calibration set of 12 solutions (Table V) has no advantages over the use of the calibration set of 9 solutions and was thus not used for practical samples of REE hydroxide concentrates. The error attained in predicting the concentrations of the individual components, CRPE, of less than 10 rel.% can be considered as good, considering the considerable overlap of the absorption spectra of the ternary complexes of the individual components. At pH 5.5 the greatest error accompanied the determination of Al, as the absorption maximum of the Al complex lies between the absorption maxima of the Th and Fe complexes. The correctness of the determination is thus affected by two components simultaneously. The determination of Th is accompanied by a larger error than the determination of Fe, apparently as a consequence of the greater absorbance of the reagent in the wavelength region important for the determination of Th. At pH 10.2, the lowest error was found for the determination of the sum of the REE, apparently as a result of the fact that the conditions for the analysis (especially the pH for the formation of the ternary complexes) are optimal for the determination of the sum of the REE.

The results for the determination in the combined system (pH 5.5 + pH 10.2) are comparable with the results obtained in the separate systems and are even better for some components (Al, Fe, Th). It is thus useful and advantageous to carry out multicomponent analysis directly for all 4 components in combined data with the data system.

The determination of the possibility and advantages of combining two (several) experimental systems with completely different component concentrations in a single data set is the main contribution of this work.

Reduction of the Number of Wavelengths

A reduction in the number of wavelengths (Table VI) does not have such great consequences in increasing the error in the predictions for the individual components as does a decrease in the number of calibration solutions (Table V), caused especially by the fact that the number of wavelengths is decreased evenly, which practically does not change the selectivity of the system. The error in the determination on a decrease in the number of wavelengths is less for the combined data system.

It follows from the results that the ability to carry out the measurement for a smaller number of wavelengths leads to considerable time savings while retaining an acceptable error level in the determination of the concentrations of the individual components.

Analysis of Hydroxide Concentrates of the Rare Earth Elements

The results obtained in analysis of hydroxide concentrates of REE (Table VI) confirm the conclusions drawn from the model sample (Tables V and VI). The relative errors in the determination of the individual components CRPE are again less than 10 rel.%.

The results obtained permit us to draw the conclusion that all 4 components (Al, Fe, Th and the sum of the REE) can be determined in practice in a concentration range of 1 – 1.5 orders on the basis of measurement of 9 calibration solutions at pH 5.5 and 10.2, at 18 or only 10 wavelengths, with evaluation of the combined data set.

For the multicomponent determination of Al, Fe, and Th in hydroxide concentrates of the rare earth elements, it is sufficient to carry out the measurement only at pH 5.5 for 9 calibration solutions and 9 wavelengths.

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